



(11) CA

No. 797,911

(65)

ISSUED Oct. 29, 1968

(52)

CLASS 401-37  
C.R. CL.

(1C)

# CANADIAN PATENT

(14)

POLYURETHANE PREPOLYMERS

*Corresponds  
to  
DE 1,595,273*

Samuel Kaizerman, New Brunswick, New Jersey, U.S.A., and  
Eugene Yue Chieh Chang, Somerville, New Jersey, U.S.A.

Granted to American Cyanamid Company, Stamford, Connecticut,  
U.S.A.

*Dist.*

(21)

APPLICATION No. 961,500

(22)

FILED

May 27, 1966

(3C)

PRIORITY DATE June 23, 1965 (466,426) U.S.A.

No. OF CLAIMS 10 - No drawing

The invention relates to a process for making an improved is cyanate-terminated polyurethane prepolymer substantially free from unreacted diisocyanate. It also relates to a process for reacting a polymeric ether glycol or polymeric ester glycol with a large excess of a diisocyanate, followed by a distillation step to remove substantially all of the unreacted diisocyanate.

As employed in the polyurethane art and in this specification as well, the term "prepolymer" is intended to mean a low molecular weight polymeric reaction product of a molar excess of a diisocyanate compound with either 1) a hydroxy-terminated polyester or 2) a polyalkylene ether glycol or 3) a combination of 1) and 2). The reaction product is actually a complex mixture of some unreacted starting material, and, mostly, addition products derived from one or more diisocyanate molecules and one or more polyester or polyether molecules.

Prepolymers are converted to polyurethanes by "curing" with isocyanate-reactive compounds such as glycols or diamines. The curing step is generally accomplished by charging a thoroughly blended mixture of prepolymer and curing agent into a mold where, after heating for a time, curing is achieved. Several qualifications must be met by a prepolymer for it to be suitable in commercial polyurethane operations.

The prepolymer must be of sufficiently low viscosity to be flowable at temperatures below the decomposition temperature. Preferably, the low viscosity should be attainable with only mild application of heat.

The prepolymer should be almost completely devoid of hydroxy termination. This is to say sufficient isocyanate should have been reacted with the polymeric ether or ester glycol to assume that substantially each hydroxyl group has combined with an isocyanate group.

The prepolymer must have a sufficiently long pot-life

at normal and elevated temperatures to remain fluid and reactive during the time between admixture with the curing agent and charging into the mold or extruder, etc., used in preparing the shaped polyurethane product. This is of considerable practical importance since even efficient and continuous operations are subject to unexpected hold-ups, and even some scheduled shut-downs. Moreover, in storing the prepolymer and curing agent mixture for so-called "immediate" use, it is reasonable to assume that while prepolymer is charged and discharged from the storage tank at equal rates, some significant amount will have a longer tank residence than the short time it takes to flow directly through the tank. The prepolymer-curing agent mixture must be able to retain its properties through this delay also.

Prepolymers which partially satisfy all of the foregoing requirements, to some extent, are presently available, as witnessed by the large commercial production of polyurethanes. This is not to say that there is no room for improvement, for the fact is that plenty does exist in respect to increasing the pot-life (or "gelling time") and reducing the viscosity of the prepolymer without sacrificing other desirable properties of the material.

It is an object of the present invention to provide an improved process for producing a prepolymer which has both a long pot-life and low viscosity and is capable of being converted to an excellent polyurethane through conventional curing treatments. It is a further object of this invention to provide the prepolymer which results from the foregoing process. Other objects will become apparent from the ensuing description of the present invention.

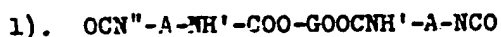
The present invention is based upon the discovery that a prepolymer of excellent properties is obtained by reacting a larger-than-usual excess of diisocyanate with glycol (either polyether or polyester type) and then removing substantially

all of the unreacted diisocyanate from the crude prepolymer before the latter is contacted with a curing agent. Preferably, distillation means are employed to effect the desired end.

A superior, isocyanate-terminated prepolymer is obtained when the unreacted diisocyanate is removed from the prepolymer obtained by reacting a polymeric glycol with an excess of diisocyanate. It is important to note that a prepolymer with the above-named advantages is obtained only if both a large excess of diisocyanate is used in the formation of the prepolymer and substantially all of the unreacted diisocyanate is then removed. The upper limit of free diisocyanate concentration remaining after distillation is a critical aspect of this invention.

While it is not intended to link the scope of this invention to any theoretical explanation thereof, it may be of value in gaining an understanding of the invention to be aware of certain hypothetical considerations.

The reaction between the diisocyanate and the glycol can and does proceed along two basic patterns. Thus, if a molar excess of diisocyanate ( $\text{OCN}'\text{-A-N}''\text{CO}$ ) is contacted with a glycol ( $\text{HO-G-OH}$ ) under reactive conditions, the reaction product contains the following type of compounds:



In the foregoing, "A" is the residue of a diisocyanate (especially an aromatic one such as tolylene 2,4-diisocyanate), "G" is the residue of a polyglycol (either polyether or polyester) and "n" is an integer of one to about 10. The greater the content of "1" in the prepolymer, the lower the viscosity. The greater the content of "2", especially when "n" is larger than two, the higher the viscosity of the prepolymer and the less desirable it is for commercial preparation of polyurethanes. The desired formation of "1" is favored by increasing the molar excess of di-

is cyanate to polyglycol. As the molar ratio of diisocyanate to glycol in the reaction mixture is increased, the viscosity, which is proportional to the molecular weight of the resulting prepolymer, is lowered. It is postulated that this effect is due to a difference in reactivity between the isocyanate groups in a given molecule (i.e., a first and a second order reactive rate), and the mass action effect which increases the chances that, as the reaction proceeds, the free remaining hydroxyl groups of the polyglycol will react with isocyanate radicals of first order reactivity. This means that the chances of forming a long molecule of "n" polyglycol moieties joined by "n" isocyanate moieties are reduced as compared to the chances of forming low molecular weight isocyanate-terminated polyglycols.

If it is attempted to prepare a prepolymer of low viscosity by loading the reaction mixture with excess diisocyanate, the attempt is successful insofar as viscosity is concerned, but the prepolymeric material is nevertheless precluded from commercial use because of a very short pot-life. In other words, upon admixture of the prepolymer with curing agent, curing is so rapid as to make impractical the handling of such a product on a commercial scale.

The innovation of removing unreacted diisocyanate permits the use of larger-than-normal amounts (excesses) of diisocyanate in the reaction with the polymeric glycol. When large excesses of diisocyanate, e.g. tolylene diisocyanate (TDI), are used and the unreacted diisocyanate is removed, the resulting prepolymer has a lower viscosity than that obtained when the customary amount of diisocyanate is used. Prepolymers with lower viscosities are desirable for use in molding and coating operations. In addition, the prepolymer is advantageously found to have a long pot-life.

At this point, it may be well to explain what is meant by the expression "excess diisocyanate" in terms of the amount

of polyglycol used to form the prepolymer. Each diisocyanate molecule has two reactive isocyanate groups and each polyglycol molecule has two reactive hydroxyl groups. The aim in forming the prepolymer is to terminate each glycol molecule with a reactive isocyanate group. Theoretically, therefore, each mole of glycol should react with two moles of diisocyanate. In actual practice, however, a certain proportion of the diisocyanate will react at both isocyanate groups, resulting in the joining of two glycols. This latter reaction requires a 1:1 ratio of diisocyanate to glycol. On account of these two types of reactions, a ratio of about 1.1 to about 1.7 moles of diisocyanate to each mole of glycol, will normally leave substantially no unreacted diisocyanate in the reaction product. Any prepolymer with less than about 0.5% and preferably less than 0.3% by weight of unreacted diisocyanate is considered free of the same. Whether 1.7 moles of 1.1 moles of diisocyanate can fully react, depends on which isocyanate is used. Pure 2,4-TDI, for example, can react in a ratio of about 1.7:1.0 with glycol; an 80:20 mixture of 2,4-TDI-2,6-TDI can react in a ratio of about 1.6 to 1.0 with glycol. Other diisocyanate compositions react in different molar ratios. Whatever the diisocyanate, it is considered to be used in excess if, under reaction conditions, the prepolymer product will contain more than 0.5% of unreacted diisocyanate.

The product prepared by the present invention is readily distinguishable from products which are made by different, though apparently related, processes. In U. S. Patent 3,183,112, there is disclosed a process of making a prepolymer whereby excess diisocyanate is reacted with an "alcohol" containing one to four hydroxyl groups. The alcohol may be polymeric but is generally only a monomer. The patentee teaches the removal of excess diisocyanate from the reaction product so as to leave less than 2% of free diisocyanate in the product. The products of the patent are taught to be as useful as lacquers. The distinction

between the present invention and the teaching of U. S. Patent 3,183,112 lies in the definition of "excess" diisocyanate. In the patent, an acceptable product for lacquer usage is obtained when over 0.5% and up to 2% of free diisocyanate is present even after distillation. The patentee teaches that over 2% leads to odor and toxicity problems in the lacquer product. For purposes of forming lacquers, there is no disclosure in the patent of the need or desirability of reducing the free diisocyanate content to below 0.5%.

10           The crude prepolymer which is obtained by contacting excess diisocyanate and glycol under reaction conditions is freed of unreacted diisocyanate by any process which is capable of doing so. A typical and effective means to achieve this end is to distill the crude prepolymer at a temperature below 225°C., and preferably, below 175°C. Normally, distillation should be conducted in vacuo (10 mm. or less of Hg.) to thereby permit use of lower distillation temperatures. Conventional distillation means, preferably that which permits rapid removal of the diisocyanate, including flash distillation apparatus, can be used for this purpose. After distillation, the prepolymer product should have no more than about 0.3%, and preferably less than about 0.25% of free diisocyanate.

20           The difference between a prepolymer prepared by the process of this invention, and one in which unreacted diisocyanate has not been removed, is demonstrable by a test in which a conventional amine curing agent, 3,3'-dichloro-4,4'-diaminodiphenylmethane, termed "MOCA" for brevity, is used to cure the prepolymer under a standard set of conditions. The time required for the prepolymer to cure to a viscosity increase of 50,000 cps. is noted. The shorter the time, the less desirable the product is for commercial use.

30           The polymeric glycols of use in this invention have a molecular weight of at least about 500 and normally less than

797911

about 5,000. Useful glycols can be either polyester glycols or polyalkylene ether glycols. The polyester glycols are the condensation products of diols of about two to ten carbon atoms and dicarboxylic acids of about two to eight carbon atoms in each alkylene chain. The alkylene linkages in both the polyesters and the polyethers may be straight or branch-chained.

The polyesters include those prepared from (1) glycols such as ethylene glycol, propylene glycol-1,2, propylene glycol-1,3, butylene glycol-1,4, decamethylene glycol and mixtures thereof, and (2) dicarboxylic acids, such as succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid and mixtures thereof.

The polyethers include polyethylene ether glycol, polypropylene ether glycol, polytetramethylene ether glycol, poly-1,2-dimethylethylene ether glycol and mixtures thereof.

The diisocyanates of use in the process of this invention include all the diisocyanates normally used in making polyurethanes. Normally those diisocyanates are preferred which are sufficiently volatile to be removed by distillation below the temperature of 225°C. at 0.1 mm. Hg. A preferred diisocyanate is tolylene diisocyanate (TDI). Others which may be used are hexamethylene diisocyanate, m-xylylene diisocyanate, bis(2-isocyanatoethyl)carbonate and m-phenylene diisocyanate.

The advantages of this invention are evident when the molar ratio of diisocyanate to polymeric glycol in the prepolymer reaction mixture is as low as 1.5:1, but for greatest effect, the ratio should be at least 1.7:1 and preferably at least 2.0:1. The upper limits of diisocyanate usage are largely determined by economics, but ratios as high as 7:1 may be used.

The reaction between polymeric glycol and diisocyanate is carried out in a conventional manner. A stabilizer such as adipoyl chloride may be used if desired.

The prepolymers obtained by the procedure of this in-

vention can be cured by reaction with (1) amines such as 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA) and 3,3'-dichlorobenzidine (DCB), (2) glycols such as hydroquinone bis(hydroxyethyl) ether (PEHQ) and 1,4-butanediol (BDO) and (3) combinations of amines and glycols, e.g. MOCA and BDO.

In a preferred embodiment of this invention, one mole of hydroxy-terminated poly(ethylene adipate) having a molecular weight of about 1250, an acid number of less than one and a hydroxyl content of about 2.7% is reacted under normal conditions with about 2.1 moles of 2,6-2,4-tolylene diisocyanate. The unreacted diisocyanate is then distilled from the prepolymer at an elevated temperature under reduced pressure using a thin film evaporator. The NCO radical content of the final prepolymer is about 4.3%. This figure can be used as an indication of the average molecular weight of the products since the number of NCO groups divided by two is equal to the number of molecules of prepolymer.

In the following Examples, the parts and percentages are by weight.

20

#### EXAMPLE 1

A hydroxy-terminated poly(ethylene adipate) (2500 parts, 1.68 mole) with molecular weight of 1490 is reacted with tolylene diisocyanate (729 parts, 4.18 moles) in the presence of adipoyl chloride (0.5 part) for four hours at 50-70°C. (The molar ratio of diisocyanate to polyester is 2.5/1.0). The resulting prepolymer, having a total NCO content of 6.5% and containing a considerable amount of unreacted tolylene diisocyanate, is subjected to a distillation operation using a thin-film evaporator. The distillation is carried out at a temperature of 127-135°C. and a pressure equivalent of 0.6-0.8 mm. of mercury. In the thin-film evaporator, the residence time of the prepolymer is about 1.5 minutes. The amount of tolylene diisocyanate removed by the distillation process is about 4.9% by weight of the

30

original polymer. The resulting prepolymer has a total NCO content of about 4.22%, a MOCA gel time of about 12.5 minutes at 80°C., a viscosity of 3073 cps. at 70°C. and contains essentially no unreacted tolylene diisocyanate, as indicated by freedom from odor of tolylene diisocyanate.

The "MOCA gel time" is determined by mixing the prepolymer and MOCA at the stated temperature and noting the time required for the viscosity of the mixture to increase to 50,000 cps.

As compared to the prepolymer of Example 1, a prepolymer prepared by the same procedure except for the omission of the distillation step, has a total NCO content of 6.0%, a MOCA gel time of about four minutes at 80°C. and a strong odor of tolylene diisocyanate.

#### EXAMPLES 2-4

The procedure of Example 1 is followed with the variations shown in Table I.

TABLE I

Example	2	3	4
Poly(ethylene adipate)			
Molecular weight	1400	1520	1520
Parts	2500	2500	2500
Moles	1.79	1.65	1.65
Tolylene Diisocyanate			
Parts	700	788	860
Moles	4.02	4.53	4.95

797911

TABLE I Cont'd

Example	2	3	4
Ratio TDI/Polyester	2.25/1	2.75/1	3.0/1
Initial NCO, %	5.84	7.31	8.26
Distillation Conditions			
Temp., °C.	131-137	127-135	130-140
Pressure, mm. Hg.	0.8	0.5-0.6	0.5-0.6
Residence Time, min.	1.25	1.4	1.5
TDI Removed, %	3.8	7.2	8.3
Prepolymer Properties			
NCO, %	4.18	4.26	4.50
Viscosity, cps. at 70°C.	3179	2595	2358
MOCA gel time at 80°C. min.	12	14	11.5

EXAMPLE 5

A prepolymer prepared by the procedure of Example 1 using a polyester with a molecular weight of 1090 and a TDI/polyester ratio of 1.83/1.0, is subjected to a distillation operation by passing the prepolymer twice through a thin-film evaporator. The product has a NCO content of 4.22%, a viscosity of 4238 cps. at 70°C. and a MOCA gel time of 14.25 minutes at 80°C.

The Example shows the use of a low ratio of TDI to polyester with resultant higher viscosity of prepolymer.

EXAMPLE 6

797911

A hydroxy-terminated poly(ethylene adipate) (613.5 parts, 0.466 mole) with molecular weight of 1050 is reacted with tolylene diisocyanate (206 parts, 1.18 moles, TDI/polyester ratio 2.5/1.0). The resulting prepolymer is subjected to a distillation operation using conventional distillation equipment. The distillation is carried out for about 60 minutes at 125°C. and a pressure equivalent to 0.08 mm. of mercury. About 4.8% of TDI is thereby removed. The final prepolymer has a NCO content of 4.74 and a viscosity of 2380 cps. at 70°C.

10

EXAMPLE 7

A polypropylene ether glycol (2050 parts, 2.0 moles) with molecular weight of 1025 is reacted with tolylene diisocyanate (1220 parts, 7.0 moles) for 48 hours at 30°C. (The molar ratio of diisocyanate to polyether is 3.5/1.0). The resulting prepolymer is subjected to a distillation or stripping operation using a thin-film evaporator under high vacuum. The resulting prepolymer has a total NCO content of about 6.15%, a viscosity of 564 cps. at 70°C. and a MOCA gel time of about five minutes at 80°C.

20

For comparison, the product from the same raw materials, but using 3.5 moles of diisocyanate and omitting the distillation step, has a NCO content of 4.6%, a viscosity of 1259 cps. at 70°C. and a MOCA gel time of about four minutes.

EXAMPLE 8

25

This Example demonstrates the difference in gel times of a prepolymer product in which less than 0.5% free diisocyanate is present as compared with a prepolymer containing 1.26% free diisocyanate.

30

To 375 parts (2.15 moles) of tolylene diisocyanate (80/20 mixture of the 2,4- and 2,6-isomers) are added 2000 parts (1.0 mol) of a hydroxyl-terminated poly(ethylene adipate) of molecular weight 2000. The addition is made over a period of three hours while maintaining the temperature of the reaction

797911

mixture at 60°C. After addition is complete, the reaction mixture is heated to 75°C. and held at this temperature for 2 hours. The reaction mixture is then distilled at 149-153°C. using a thin-film evaporator and a pressure equivalent to less than 0.5 mm. of mercury. The prepolymer obtained has an -NCO content of 2.97% and contains 0.26% of free diisocyanate.

A portion of the prepolymer obtained above is mixed with a stoichiometric quantity of 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA) at 100°C. The pot-life is 12.5 minutes.

To another portion of the prepolymer obtained above is added 1% of the diisocyanate removed as distillate (the distillate is a 30/70 mixture of 2,4- and 2,6-tolylene diisocyanates) making the total free diisocyanate content equal to 1.26%. Upon addition of MOCA as above, the pot-life is 6.5 minutes. This Example shows the criticality of the free diisocyanate content upon pot-life of those prepolymers which are useful as elastomers.

It is immaterial with respect to pot-life whether the free diisocyanate is added to the distilled prepolymer or left in the prepolymer by inadequate distillation.

797911

The embodiments of the invention in which an exclusive property or privilege is claimed, are defined as follows:

1. A process for the preparation of a prepolymer having relatively low viscosity and improved pot-life, which comprises bringing into reactive contact a mole of a polyglycol having a molecular weight of about 600-2,000 and with at least about 1.5 moles of an aromatic diisocyanate, thereby forming an isocyanate-terminated prepolymer having more than 0.5% of unreacted aromatic diisocyanate; treating the crude prepolymer thus obtained in a manner such that no more than 0.5% of unreacted diisocyanate is present in the prepolymer.
2. The process of Claim 1 wherein at least two moles of aromatic diisocyanate are used for each mole of polyglycol.
3. The process of Claim 1 wherein the unreacted diisocyanate is removed from the crude prepolymer by distillation under reduced pressure at a temperature below about 225°C.
4. The process of Claim 1 wherein the glycol is a hydroxy-terminated polyester having a molecular weight in the range of about 1,000-2,000.
5. The process of Claim 4 wherein the polyester is poly(ethylene adipate) glycol.
6. The process of Claim 1 wherein the glycol is a polyether.
7. A process for preparing a prepolymer of relatively low viscosity and long pot-life which comprises bringing into reactive contact at least 2.0 moles of 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate or mixtures of said diisocyanates, and one mole of poly(ethylene adipate) glycol having a molecular weight between 600 and 2,000, to thereby form a crude prepolymer reaction product having more than 0.5% of unreacted diisocyanate; and distilling the reaction product at a temperature below about 225°C. and under reduced pressure thereby reducing the unreacted diisocyanate content to below 0.5%.
8. The product prepared by the process of Claim 1.
9. The product prepared by the process of Claim 2.

10. The product prepared by the process of Claim 7.